



DEPARTMENT OF THE ARMY
CORPS OF ENGINEERS, OMAHA DISTRICT
215 NORTH 17TH STREET
OMAHA, NEBRASKA 68102-4978

September 25, 1989

REPLY TO
ATTENTION OF

Environmental Branch

4.2
Superfund Records Center
SITE: New Bedford
BREAK: 7.2
OTHER: _____

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OCT 04 89

Mr. Frank Ciavattieri
U.S. Environmental Protection Agency
Region I
90 Canal Street
Boston, Massachusetts 02203

Dear Mr. Ciavattieri:

Enclosed for your information is one copy each of the following memoranda:

Memorandum for Record, April 1989, subject: Laboratory Assessment of Volatization from New Bedford Harbor Sediment, by Dr. James Brannon (encl 1).

Memorandum for Record, August 22, 1989, subject: Theoretical Models for Volatile Emissions from Dredged Material-Comparison of Predicted and Laboratory Measurements for New Bedford Harbor Sediment, by Dr. Louis J. Thibodeaux (encl 2).

Transmittal of this information completes the U.S. Army Corps of Engineers efforts in evaluation of volatile emissions from New Bedford Harbor dredged material. If you have any questions, please contact Mr. Kevin Mayberry of my staff, at (402) 221-7820.

Sincerely,

S. L. Carlock, P.E.
Chief, Environmental Branch
Engineering Division

2 Encl

SDMS DocID 000200526



April 1989

MEMORANDUM FOR RECORD

SUBJECT: Laboratory Assessment of Volatilization From New Bedford Harbor Sediment

Introduction

1. A confined disposal facility (CDF) is a diked area for gravity separation and storage of dredged material solids. When contaminated dredged material is placed in a CDF, the potential exists for volatile organic chemicals associated with the sediment to be released to the air. Sediments from the New Bedford Harbor Superfund Site, New Bedford, MA, contain significant amounts of polychlorinated biphenyls (PCBs), some of which may be released to the air during evaporative drying in a CDF.

2. Models for evaluation of volatile emissions to air during dredged material disposal have been developed under contract to the US Army Engineer Waterways Experiment Station (USAEWES)*. These theoretical models may be applied to calculate potential volatile PCB emissions from CDFs proposed for containment of New Bedford Harbor sediment. However, field or laboratory data suitable for comparison to model predictions have not previously been available. The USAEWES has completed a laboratory study that measures volatile emission rates of PCBs from New Bedford sediment. The US Environmental Protection Agency, Region I, provided funding for this work through the US Army Engineer District, Omaha.

3. This MFR summarizes the laboratory results obtained from measurement of volatile emissions of PCBs from New Bedford Harbor sediment. Emphasis is on development of laboratory procedures, trends in volatile emissions as a function of evaporative sediment drying, and comparison of measured laboratory fluxes with those predicted by the theoretical models.

Methods

4. The emission isolation flux chambers (volatilization chambers) utilized are illustrated in Figure 1. The bottom of the flux chamber is ordinarily open to facilitate placement over sediment; however, for this laboratory study a false bottom was inserted into the chamber so that a 2.5 cm depth of sediment could be placed into the chamber prior to each experiment. Surface area and volume of the chamber was 0.146 square meters and 0.024 cubic meters, respectively. The carrier gas was air, at 10 psig. The chamber was made of stainless steel and did not have an impeller for internal mixing. The interior of the chamber top was rinsed with hexane between each run. A complete description of the volatilization chamber can be found in

* Thibodeaux, L.J. (1989). "Theoretical Models for Evaluation of Volatile Emissions to Air During Dredged Material Disposal with Applications to New Bedford Harbor, Massachusetts", Miscellaneous Paper EL-89- , US Army Engineer Waterways Experiment Station, Vicksburg, MS.

minimized PCB breakthrough into the second column. The highest mass of Aroclor 1242 was recovered at the 900 cc/min flow rate without the pronounced breakthrough into the second column observed at higher flow rates.

9. Table 4 presents results from experiment 3 conducted to obtain an estimate of the variability of the apparatus and experimental procedures utilized. Volatilization runs were conducted sequentially following loading of fresh sediment. As shown in Table 5, only the emission rate in the second 30 min run differed substantially from emission rates measured in the other runs. The reason for the deviation of the second 30 min run from the other values was not readily apparent.

10. Volatilization rates of PCBs, and PCB mass on the florosil columns as a function of evaporative sediment drying are summarized in Tables 6 and 7, respectively. Total PCB volatilization rate and sediment porosity as a function of time are illustrated in Figure 4. Data were obtained by loading one inch of New Bedford sediment into the apparatus and measuring PCB volatilization for one hour at a flow rate of 900 cc/min at intervals over a period of 10 days. The apparatus cover was removed and the sediment allowed to dry between measurements. Concurrently with the measurement of PCB volatilization, the porosity and moisture content of sediment in an identical setup (Table 6) were measured. Depth and width of cracks developing in the sediment during drying were also measured. No cracks were observed during days 1 and 2 of the experiment. One small 9-cm crack 2 mm deep was observed on day 3. At day 4 the small crack had deepened to the floor of the chamber and numerous smaller cracks had appeared. By day 5, cracks extended over the entire sediment area and to the floor of the chamber. Results from this experiment indicated that PCB volatilization peaked immediately following loading, decreased, and then developed a smaller peak as surface area increased due to cracking. Most PCB congeners measured during the experiment possessed a low degree of chlorination, confirming that they volatilize more readily than congeners with a high degree of chlorination. It was also noted that the volatilization rate measured on fresh sediment (day 1) during this experiment were lower than rates reported in earlier experiments in this study. As shown in Table 8, the lower volatilization rates were also observed in experiments 4 and 6 which were conducted during the same time period. The reasons for these lower volatilization rates are not readily apparent. Neither analytical standards, computational procedures, nor sediment were varied. Some losses during sediment mixing prior to addition to the volatilization chamber are expected, but not sudden, reproducible losses of the magnitude measured.

11. Losses of PCB by adsorption within the apparatus are illustrated in Table 9. The mass of PCB adsorbed to the stainless steel lid of the volatilization apparatus was measured following a one hour run. Therefore, the procedures used probably underestimated the volatilization rates.

12. A simple capping evaluation was conducted using a 2.5 cm cap of noncontaminated, readily available sediment from a small lake on the premises of the USAEWES (Brown's Lake). The capping evaluation was not successful due to operational problems resulting from use of such a thin cap, i.e. incomplete isolation of the contaminated material. PCB release rates measured from the capped treatment were 4.85 ug Aroclor 1242/meter square/hr compared to 5.67 ug Aroclor 1242/meter square/hr for uncapped material. Brown's Lake sediment yielded chromatographs identical to the blank.

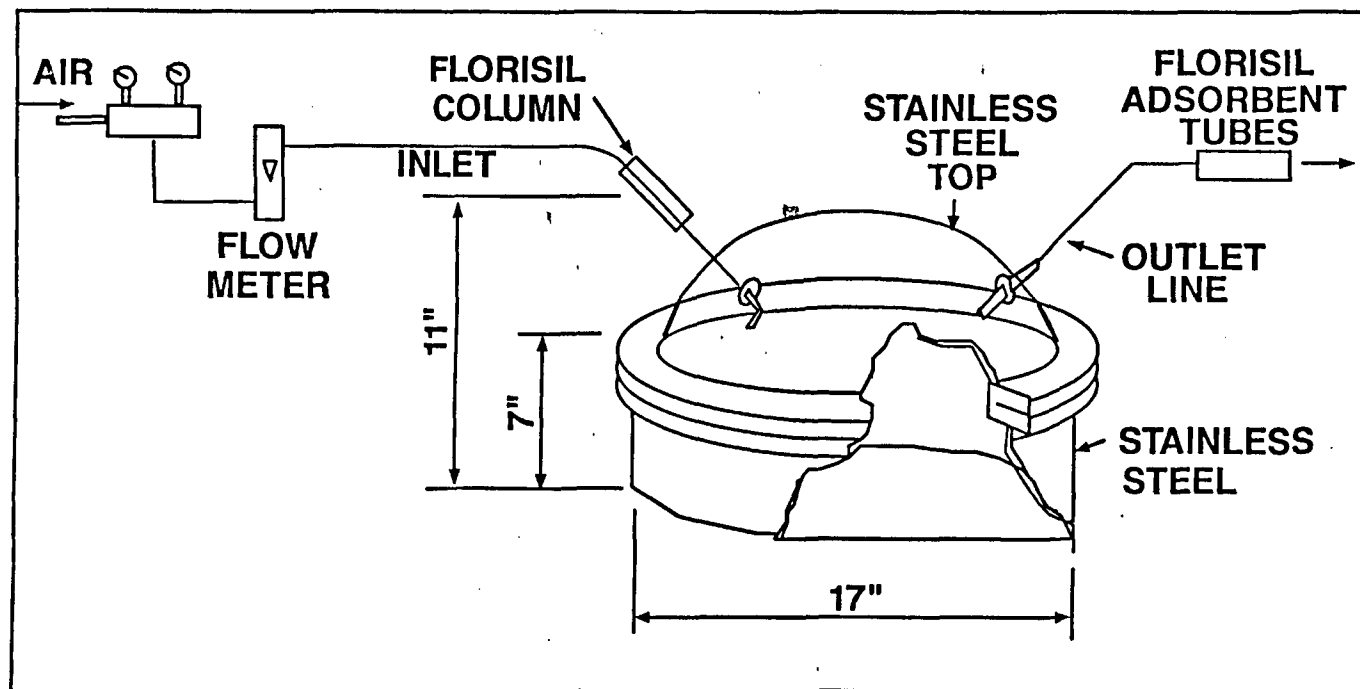


Figure 1. Volatilization Measurement Apparatus

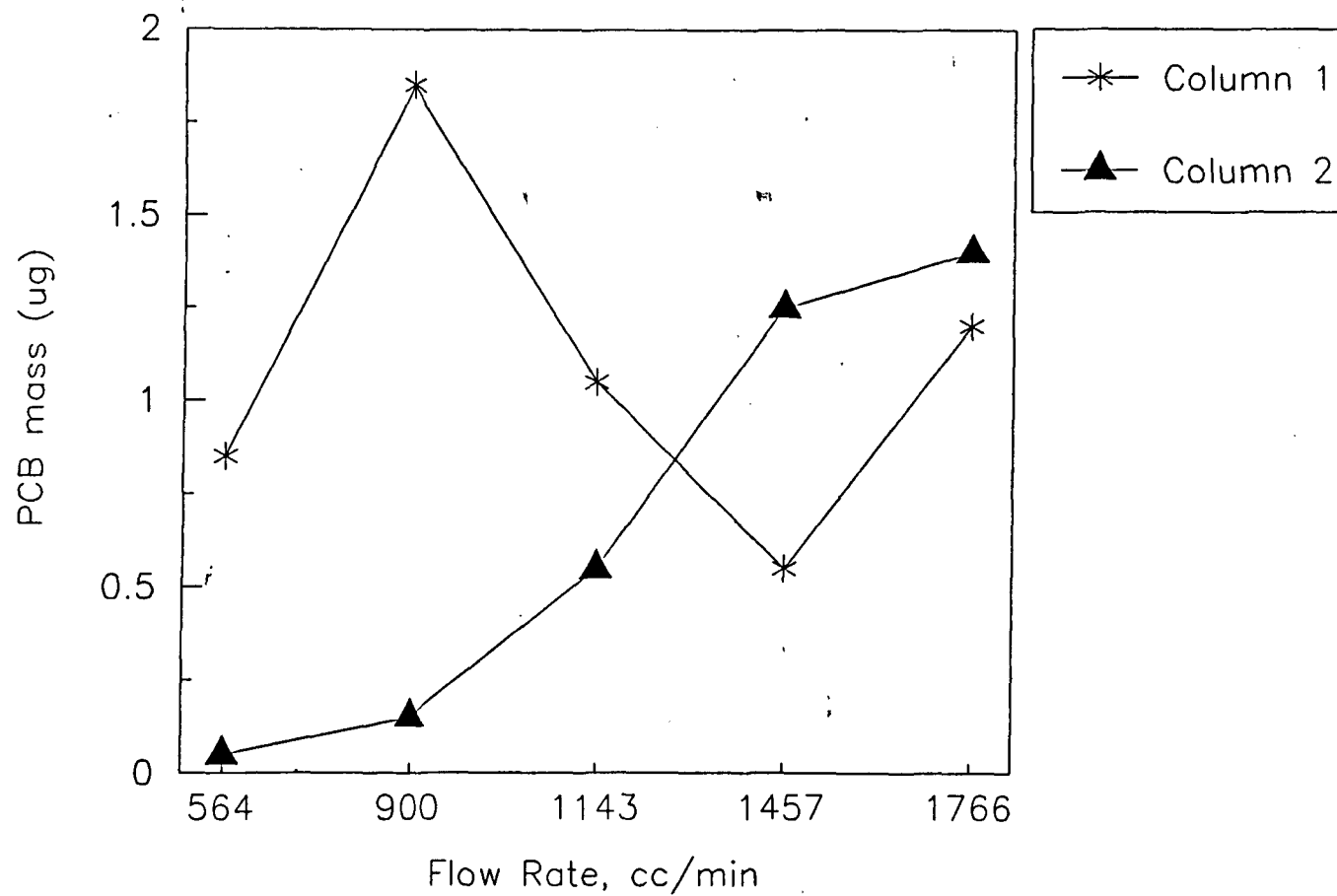


Figure 3. PCB Aroclor 1242 Mass collected on Adsorption Columns Connected in Series as a Function of Flow Rate.

Table 1. List of experiments conducted during this study.

Experiment Number	Experimental Purpose
1	Determine the number of adsorption columns in a series needed to trap PCB emissions
2	Determine the effects of flow rate on PCB recovery
3	Estimate the variability of the experimental procedures
4	Determine the optimum methylene chloride:hexane ratio for desorbing PCBs from adsorption columns prior to analysis
5	Determine the effects of evaporative sediment drying on PCB emissions
6	Determine if a one inch cap is effective in preventing emission of PCBs from New Bedford Harbor sediment

Table 3. Effect of flow rate on PCB releases (ug). Run time of 30 min.
Volatilization rates (ug/m²/hr) are in parentheses.

PCB compound	Column*	Flow Rate (cc/min)				
		564	900	1143	1457	1766
Aroclor 1242**	1	0.85 (11.6)	1.85 (27.3)	1.05 (22.5)	0.55 (24.6)	1.20 (35.5)
	2	BDL+	0.15	0.55	1.25	1.40
Congener 8	1	BDL	0.025 (0.34)	0.01 (0.14)	0.005 (0.07)	0.020 (0.5)
	2	BDL	BDL	BDL	BDL	0.015
Congener 44	1	BDL	0.015 (0.10)	BDL	0.015 (0.27)	0.005 (0.27)
	2	BDL	BDL	BDL	0.005	0.015
Congener 49	1	0.015 (0.20)	0.045 (0.6)	0.030 (0.4)	0.050 (0.75)	BDL (0.9)
	2	BDL	BDL	BDL	0.005	0.065
Congener 50	1	0.030 (0.4)	0.080 (1.1)	0.070 (1.0)	0.095 (1.3)	BDL (0.2)
	2	BDL	BDL	BDL	BDL	0.014
Congener 52	1	0.010 (0.14)	0.040 (0.55)	0.030 (0.5)	0.045 (0.75)	0.010 (0.14)
	2	BDL	BDL	0.005	0.010	0.065
Congener 77	1	BDL	0.025 (0.34)	BDL	BDL	BDL
	2	BDL	BDL	BDL	BDL	BDL

* Column 1 and 2 were set up in series.

** All PCB measured was aroclor 1242; therefore, aroclor 1242 and total PCB concentrations are the same.
All blanks were below detection limits.

+ BDL = Below Detection Limits (0.05 ug for Aroclors and total PCB; 0.005 ug for congeners).

Table 5. Emission rates ($\mu\text{g}/\text{m}^2/\text{hr}$) computed from data in Table 4.

Run	Time	Compound						
		Aroclor 1242	Con 8	Con 44	Con 49	Con 50	Con 52	Con 77
1	30 min	17.8	8.9	0.07	0.55	0.82	0.34	BDL
2	30 min	60.1	3.6	0.03	0.82	1.30	0.96	0.34
3	30 min	21.2	0.82	0.14	0.55	1.23	0.61	0.14
4	1 hr	18.1	0.58	0.14	0.44	1.02	0.55	0.03

Table 7. Mass of PCB (ug) collected during volatiles run.

Time, Days	Col #	Compound								
		Blanks*	Tot PCB	C18	C28	C31	C44	C50	C101	C141
1	1	0.10	0.80	0.11	0.01	0.04	0.004	0.028	0.003	0.002
	2		0.40	0.02	0.003	0.005	BDL	0.004	0.002	BDL
2	1	0.11	0.34	0.03	0.004	0.01	BDL	0.01	0.003	0.003
	2		0.13	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3	1	0.10	0.17	0.003	BDL	BDL	BDL	BDL	BDL	BDL
	2		0.013	BDL	BDL	BDL	BDL	BDL	BDL	BDL
4	1	0.11	0.05	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	2		0.22	BDL	BDL	BDL	BDL	BDL	BDL	BDL
5	1	0.17	0.25	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	2		0.23	BDL	BDL	BDL	BDL	BDL	BDL	BDL
7	1	0.10	0.24	0.01	0.002	BDL	BDL	BDL	BDL	BDL
	2		0.10	BDL	BDL	BDL	BDL	BDL	BDL	BDL
8	1	0.09	0.22	0.03	0.003	0.01	BDL	0.007	BDL	BDL
	2		0.11	0.005	BDL	BDL	BDL	BDL	BDL	BDL
10	1	0.10	0.14	0.01	BDL	0.005	BDL	0.004	BDL	BDL

* Blank values for total PCB. Total PCB values approximately equal aroclor 1242 values. Blank values for congeners were below detection limits.

Table 9. Mass (ug) of PCB compounds in hexane rinse of chamber lid interior during a 1 hour volatilization run.

PCB Compound		Mass, ug	PCB Compound		Mass, ug
Aroclor	1242	2.0	Congener	97	0.01
Aroclor	1254	0.36	Congener	101	0.031
Total	PCB	2.35	Congener	118	0.047
Congener	15	2.49	Congener	121	0.031
Congener	18	0.23	Congener	128	0.004
Congener	28	0.052	Congener	138	0.011
Congener	31	0.11	Congener	141	0.002
Congener	40	0.006	Congener	151	0.007
Congener	44	0.03	Congener	153	0.027
Congener	49	0.012	Congener	156	0.004
Congener	50	0.084	Congener	180	0.002
Congener	52	0.084	Congener	182	0.007
Congener	54	0.002	Congener	183	0.004
Congener	60	0.009	Congener	187	0.007
Congener	70	0.012			

August 22, 1989

MEMORANDUM FOR RECORD

SUBJECT: Theoretical Models for Volatile Emissions from Dredged Material-Comparison of Predicted and Laboratory Measurements for New Bedford Harbor Sediment (Contract No. DACW39-89-M-0207)

Introduction

1. A confined disposal facility (CDF) is a diked area for gravity separation and dredged material solids. When contaminated dredged material is placed in a CDF, the potential exists for volatile organic chemicals associated with the sediment to be released to the air. Sediments from the New Bedford Harbor Superfund Site, New Bedford, MA, contain significant amounts of polychlorinated biphenyls (PCBs), some of which may be released to the air during evaporative drying in a CDF.

2. Models for evaluation of volatile emissions to air during dredged material disposal have been developed.¹ These theoretical models may be applied to calculate potential volatile PCB emissions from CDFs proposed for containment of New Bedford Harbor sediment. Four locales associated with a CDF operation were identified as separate volatile sources. These locales were: the sediment (dredged material) relocation locale, the exposed sediment locale, the ponded sediment locale and the vegetation-covered sediment locale. The exposed sediment locale was ranked the highest.

3. Field or Laboratory emission data suitable for comparison to model predictions were not available for any of the locales. The USAEWES² has completed a laboratory study that measured volatile emission rates of PCBs in a simulation of the exposed sediment locale using New Bedford dredged material. The U.S. Environmental Protection Agency, Region I, provided funding for this work through the U.S. Army Engineer District, Omaha.

4. This memorandum contains the theoretical rate predictions of Aroclor-1242 from New Bedford Harbor bed sediment. Model

Encl 2

predictions and experimental measurements are compared. Emphasis is on the ability of the theoretical models to make predictions of the emission rate of Aroclor-1242 from a drying bed sediment exposed to the air under laboratory conditions. The experimental method and the measured emission rates are from Brannon².

Review of the Experimental Data

5. A series of four experiments were performed with an emission isolation flux chamber. This apparatus placed atop sediment collected the PCB vapors. The vapors were trapped on florisisil and analyzed by gas chromatography. The vapors were collected by flowing air through the chamber for one quarter to one hour time period. Emission rates were reported in $\mu\text{g A-1242 per m}^2$ per hour. Table 1 contains the data for four experiments.

6. The first three experiments were preliminary runs designed to optimize the test protocols. These were designed to determine the number of absorption tubes required to trap the PCB vapors, the air flushing rate through the flux chamber and the variability of apparatus and procedures. Two absorption tubes, an air rate of 900 cc/min and a one hour trapping time were chosen as the best operating conditions. However, Table 1 contains the data for all runs performed.

7. In general, the experiments can be placed into two classes, wet and dry. The first three experiments were performed with sediment saturated with water. These will be termed the initial period experiments or the wet sediment experiments. Experiment no. 4 experienced significant drying and cracking. Cracking commenced on day three and was fully developed by day 5. These observations suggest that the upper sediment layers were dry and had lost much moisture. Soil porosity decreased from 0.774 on day one to 0.103 on day 10. Over this period the solid fraction increased from 0.329 to .888. Large, wide cracks existed at the termination of the experiment. The volume occupied by the sediment had decreased significantly and was estimated to be of the order of 50% or less of the original volume. The laboratory was maintained at 19.7°C to 20.3°C and low relative humidity

throughout the experiment. Experiment no. 4 will be referred to as the long-term experiment or the dry sediment experiment.

Theoretical Models

8. The theoretical models used in this analysis are from Thibodeaux¹. This section is a brief presentation and review of the model that applies for the exposed sediment locale.

9. Contaminated sediment that is wet and exposed directly to the atmosphere results in the highest VOC emission rates. Volatile organics sorbed onto/into particles at the soil surface have a very short pathway to the air. The top layers eventually become depleted of the chemical. Continuing losses will come from within the soil pore spaces. The equation that applies for this transient volatilization process is B4 from Thibodeaux¹:

$$n_A = \frac{\omega_A K^* - \rho_{A1}}{\left[\frac{\pi t}{D_{A3} (1 + \rho_B / \epsilon_1 K^*)} \right]^{1/2} + \frac{1}{^3k_{A1}}} \quad (1)$$

where n_A is the emission flux from the soil in $\mu\text{g}/\text{m}^2 \cdot \text{h}$

K^* is the air-soil equilibrium partition coefficient, g/m^3

ω_A is the chemical concentration on soil, $\mu\text{g}/\text{g}$

t is time, h

D_{A3} is the diffusion coefficient of the chemical in air-filled pores, m^2/h

ρ_B is bulk soil density, g/m^3

ϵ_1 is soil air-filled porosity, m^3/m^3

$^3k_{A1}$ is the air-side mass-transfer coefficient, m/h , and

ρ_{A1} is the chemical concentration in background air, $\mu\text{g}/\text{m}^3$.

The model is for an unsaturated (with respect to water) or dry soil column. The term soil is used to mean sediment that has

been dredged and placed in a CDF with a surface exposed to the atmosphere.

10. As the soil loses its water content by evaporation and/or drainage, the air-soil equilibrium partition coefficient changes. Three water content regimes exist in soil and require as many partition coefficients. The three regimes are: wet, damp and dry. Each can be expressed by the simple equilibrium expression

$$\rho_{A1}^* = K^* \omega_A \quad (2)$$

The partition coefficient for the wet case is the ratio of Henry's constant to the soil-water equilibrium coefficient

$$K^* = H_p / K_d \quad (3)$$

and for the dry case at low soil loadings it is:

$$K^* = p_A^* M_A / B_1 R T \omega_A^* \quad (4)$$

for the dry case at low soil loadings.

Here H_p is the Henry's constant for the chemical, $m^3 H_2O / m^3$ air

K_d is the soil-water equilibrium coefficient, $m^3 H_2O / g$ soil

p_A^* is the chemical vapor pressure, atm

B_1 is a constant, dimensionless

M_A is the chemical molecular weight, $\mu g / mol$

R is the gas constant, $82.1 E-6 \text{ atm} \cdot m^3 / mol \cdot K$

T is temperature, K, and

ω_A^* is the chemical loading on soil for a monolayer coverage, $\mu g / g$.

The damp equilibrium relationship was not employed. All are from Thibodeaux¹.

Model Predictions

11. In the section in which the experimental data was reviewed it was noted that the experiments fall into two classes. These were the initial period with wet sediment and the long-term run with dry sediment. Equation 1 applies to both cases and will be used with the respective wet and dry equilibrium expressions given by Equations 3 and 4.

12. During the initial phase of the experiment evaporation time is short (i.e. $t \sim 0$) and the sediment surface is wet. If the incoming air is also PCB free Equation 1 simplifies to

$$n_A = {}^3k'_{A1} \omega_A K_w^* \quad (5)$$

where K_w^* is given by Equation (3). At 25°C it is 0.132 g/m³.

13. There are relationships available to estimate the air-side mass-transfer coefficient³. Four of these were used to estimate ${}^3k'_{A1}$ of the isolation flux chamber conditions. Based on an average air flow path length of 30 cm within the chamber and a flow cross-section area of 135 cm² the Reynolds number of the equivalent flat geometry is 44.1, indicating the flow is laminar. Based on this and the Laminar Boundary Layer Theory relationship, a ${}^3k'_{A1}$ = 30.4 cm/h was computed. Based on the chamber air volume and flow rate the mean residence time is 2.67 min. Assuming this time represents the ratio of the flow length divided by the velocity the Penetration Theory equation yields a value of ${}^3k_{A1}$ = 60.0 cm/h.

14. Since water vapor with molecular weight 18 g/mol is less dense than air with molecular weight 29 g/mol the A-1242 transport coefficient can be estimated based on gas density differences. Two correlations are available in this regard. A thermal density driven model corrected to a mass density driven form yields ${}^3k'_{A1}$ = 74 cm/h. Using a similar correlation specifically corrected for chemical transport yields

$^3k'_{A1}=96.5/ \text{ cm/h}$. Table 2 summarized the four coefficient values and the source equations.

15. Based on the range of coefficients in Table 2 the predicted emission rates for A-1242 at 25°C with a soil loading of 887 $\mu\text{g/g}$ ranges from 35.6 to 113 $\mu\text{g/m}^2\cdot\text{h}$. These values plus the experimental values for experiments 1, 2 and 3 appear in Figure 1. The experimental values ranged from 11.6 to 61.6 $\mu\text{g/m}^2\cdot\text{h}$. The average is 26.3 $\mu\text{g/m}^2\cdot\text{h}$. The predicted values are at 25°C and the measured are at 20°C however significant overlap in the ranges of the flux rates occur suggesting the wet soil portion of the model is substantially correct.

16. The soil was essentially dry by the third day. In this case time is large and Equation 1 applies as written. The air-soil partition coefficient should reflect the dry state of the soil.

17. A procedure based on the theory of gas mixtures absorbing competitively on a solid surface that extends the classical Brauner-Emmett-Teller (BET) model to account for water vapor was used to estimate K_D^* for A-1242 on dry soil⁴. A key factor in the procedure is the surface area of the soil. In the case of sediment this is determined by the fractions organic matter and clay. Table 3 contains physical data on two New Bedford Harbor sediment samples. Based on the clay and organic matter content sediment surface area $S(\text{m}^2/\text{g})$ and A-1242 mono-layer coverages, ω_A^* , were computed. These also appear in Table 3. In the calculations: $B_1=20$ with 18.4% of S active for absorption and A-1242 density of 1.5 g/cm^3 . All other A-1242 properties were from Reference 1.

18. The necessary information is available in Equation 1 to arrive at predicted values of the flux rate. Equation 4 is used for the air-soil partition coefficient and two values appear in Table 3. The working form of Equation 1 is

$$n_A = 887K_D^* / [0.097(tK_D^*)^{1/2} + 3.29] \quad (6)$$

with t in days, K_D^* in g/m^3 and n_A in $\mu g/m^2 \cdot h$. The value of $^3k_{A1}$ used was 0.304 m/h. $D_{A3} = .035\epsilon^{4/3}$, cm^2/s . A soil bulk density of 0.69 g/cm^3 and porosity $\epsilon = 0.774$ were used.

19. The predicted values for the A-1242 flux rate assuming dry soil conditions appear in Table 4. Values of the predicted flux are for $K_D^* = 0.056$ and 0.015 g/m^3 ; these along with the measured values are shown. Comparison of predicted and measured flux values should be done for t of day 3 and greater because the soil was wet or damp before this time. The average measured flux for days 3 through 10 is $0.855 \mu g/m^2 \cdot h$ with $\sigma = 0.432 \mu g/m^2 \cdot h$. predicted flux rates are 15 and 4 $\mu g/m^2 \cdot h$. At best the predicted values are 4.7 times higher than the measured values.

20. The model predicts a very weak time dependence on the rate. At day 10 the soil-side resistance accounts for only 1.1% of the mass transport resistance. The measured values also seem to display a time dependence. This behavior may be due to several factors including cracking and other soil porosity changes with time. However, it appears that K_D^* is the primary factor that controls the flux rate in this set of measurements. A value of 0.0074 g/m^3 in the model equation yields predicted flux values in line with the experimental values. The model predicted and measured values appear in Figure 1.

21. An overall mass balance indicates 2.23g of A-1242 were present initially in the isolation flux chamber. Using $1.7 \mu g/m^2 \cdot h$ as the average rate of evaporation yields 59 μg lost from the sediment in 10 days. This is 0.0026%, so the bulk of the original A-1242 remained in the soil and did not evaporate.

Conclusions and Recommendations

22. The theoretical model does a fair job in predicting the A-1242 emission rate from exposed sediment. The measured values

for wet sediment averaged $26.2 \mu\text{g}/\text{m}^2 \cdot \text{h}$ with $\sigma = 13.0 \mu\text{g}/\text{m}^2 \cdot \text{h}$. The model yielded values of 35.6 to $113 \mu\text{g}/\text{m}^2 \cdot \text{h}$ depending on the $^3k'_{A1}$ values used. The measured values for dry sediment averaged $0.855 \mu\text{g}/\text{m}^2 \cdot \text{h}$ with $\sigma = 0.432 \mu\text{g}/\text{m}^2 \cdot \text{h}$. The most sensitive parameter being K_D^* , the air-soil partition coefficient. All-in-all the theoretical model overpredicts the measured values by a factor of 1.4 to 18.

23. Additional experimental measurements are needed to reduce this range of uncertainty and explore the effects of cracking. These experiments should involve re-wetting the soil in order to observe any increase in the flux. Field measurements at a CDF site should be performed with the isolation flux chamber. Laboratory experiments should be performed and the air-soil partition coefficient, K^* , measured for damp and dry soil conditions. This critical parameter has a very weak data base⁴.

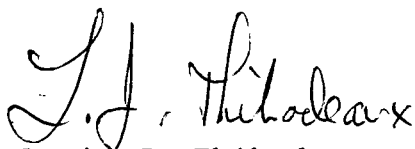
Postscript

24. The numerical values of the A-1242 vaporization flux rate reported here, both the experimental measurements and theoretical calculations, are significantly lower than the theoretical values reported earlier in Reference 1 for the exposed New Bedford Harbor sediment. For example, from the earlier report $n_A = 435 \mu\text{g}/\text{m}^2 \cdot \text{h}$ at $t=0$ for wet sediment. The average experimental measurement in this report is $26.2 \mu\text{g}/\text{m}^2 \cdot \text{h}$. Also for dry sediment at $t=10$ days the earlier reported flux is $n_A = 57.2 \mu\text{g}/\text{m}^2 \cdot \text{h}$. The average experimental measurement for dry sediment in the report is $0.855 \mu\text{g}/\text{m}^2 \cdot \text{h}$. These low emission measurements occurred even though the concentration of A-1242 in the experimental flux chamber was slightly higher than that assumed for the NBH pilot CDF (i.e., $887 \mu\text{g}/\text{g}$ vs. $207 \mu\text{g}/\text{g}$).

25. The primary reason the A-1242 vaporization rate values in this report are lower than those in the earlier report (Ref. 1), is due to the low flow rate of air in the experimental flux chamber. This low air rate forced the evaporation process to be

controlled by a laminar flow (i.e., molecular diffusion) chemical transport mechanism. Laminar flow and natural convection coefficients were calculated to be 30 to 97 cm/h. Based on the average wind speed at New Bedford and the size of the pilot CDF, the calculated coefficient was 1580 cm/h. This coefficient is larger because it reflects the turbulent chemical transport mechanism that exist in the field at this site.

26. At this time, based on the one good set of measurements available, the theoretical models presented in Reference 1 are substantially correct for low air flow and wet sediment conditions. Wet sediment is also the worst-case flux condition under turbulent air flow. Therefore, until experimental field measurements can be performed to provide a basis for refuting the algorithms and/or predictions the theoretical models developed for the NBH pilot CDF provide a rational basis for making volatile chemical emission rate estimates from exposed sediment.



Louis J. Thibodeaux
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FIGURE 1. AROCLOR 1242 VAPORIZATION RATE FROM
DREDGED SEDIMENT

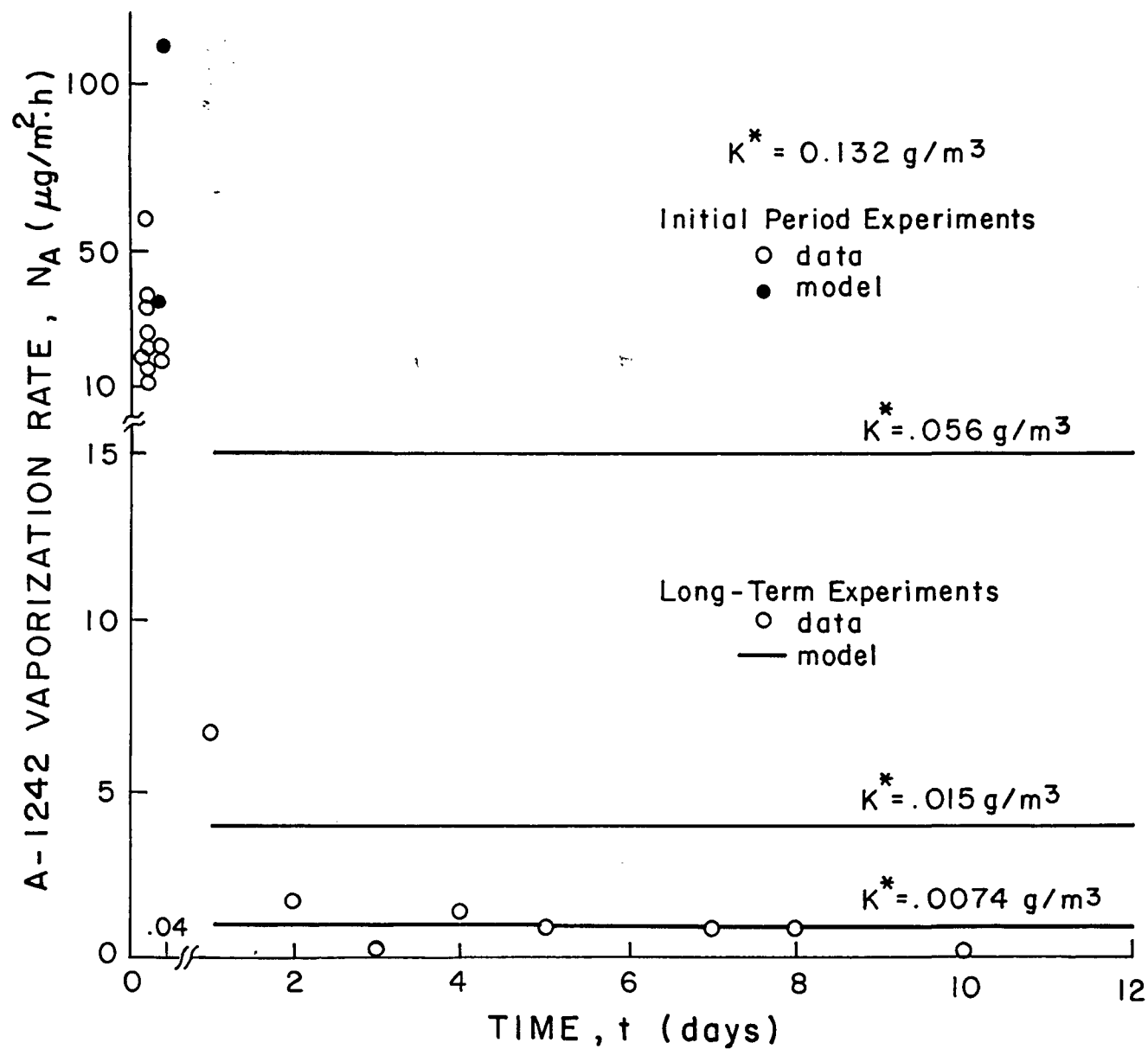


Table 1. Summary of A-1242 Emission Rates

Experiment	Time	Emission Rate ($\mu\text{g}/\text{m}^2 \cdot \text{h}$)
1 - three separate runs to determine number of absorption tubes	15 min	19.1
	30 min	33.5
	60 min	22.2
2 - five separate runs to determine air flushing rate	30 min	11.6
	30 min	27.3
	30 min	22.5
	30 min	24.6
	30 min	35.5
3 - four separate runs to determine variability of apparatus and procedures	30 min	16.4
	30 min	61.6
	30 min	22.6
	60 min	18.6
4 - long term test	1 day	6.83
	2 day	1.78
	3 day	0.48
	4 day	1.50
	5 day	0.96
	7 day	0.96
	8 day	0.96
	10 day	0.27

Table 2. Isolation Flux Chamber Coefficients

Theory	Eq. No.*	$^3k_{A1}$ (cm/h)
Boundary layer theory, laminar	41	30.4
Penetration theory	40	60.0
Heat transfer plus analogy	45	74.0
Heat transfer corrected with m-t data	50	96.5

*Source is Reference 3

Table 3. Sediment Properties

Sample	Clay*	Organic*	S	ω_A^*	K_D^*
		Matter			
	(%)	(%)	(m ² /g)	(μg/g)	(g/m ³)
Estuary Composite	0	4.48	31.4	5,290	.056
Hot Spots	12	4.48	115.	19,370	.015

*Source is Reference 5.

Table 4. Predicted vs Measured A-1242 Flux Rates
for Dry Sediment

Time (days)	n_A in $\mu\text{g}/\text{m}^2 \cdot \text{h}$		
	$K_D^* = 0.056 \text{g}/\text{m}^3$	$K_D^* = 0.015 \text{g}/\text{m}^3$	Experimental
1	15.0	4.03	6.83*
2	15.0	4.02	1.78*
3	14.9	4.02	0.48
4	14.9	4.02	1.50
5	14.9	4.01	0.96
7	14.8	4.01	0.96
8	14.8	4.00	0.96
10	14.8	4.00	0.27

*Sediment wet or damp.

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